Biological Iron Isotopic Fractionations in Antarctic Endolithic Microbial Communities

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In the McMurdo Dry Valleys, cryptoendolithic microorganisms under sandstone surfaces secrete oxalic acid to leach iron oxides from the rock. A translucent surface rock layer is necessary to allow sufficient sunlight into the endolithic habitat to support photosynthetic primary production and long-term survival. Part of the mobilized iron is re-deposited on the rock surface as a protective crust; the rest accumulates below the colonized zone. We report here that this weathering process results in redistribution of iron isotopes, with the microbial zone being enriched in heavy isotopes relative to the rock crust and the accumulation zone. In a simulated laboratory experiment to understand the cause of this isotopic effect, hematite was incubated in 5 mM oxalic acid under light. Analysis of the initial dissolved iron showed that the dissolution step could not produce the isotopic shifts observed in the rock. Presumably, equilibrium isotopic fractionation between Fe(II) and Fe(III) species is the cause, as both are produced from oxalate-promoted dissolution of iron oxides. Subsequently, microorganisms would recycle oxalate for carbon nutrient and as a result destroy iron oxalate complexes. Without chelation, the ferric iron, which is isotopically heavier, would precipitate first and ferrous iron later as they are transported downward through the circumneutral endolithic environment, effectively achieving a physical separation of the different isotopes. On Mars, if endolithic microorganisms had occurred and then became extinct as the planet dried and cooled, their iron isotopic biosignatures might be well preserved because subsequent reworking of iron would be unlikely without liquid water.